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LUBRICATING OIL COMPOSITION

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The present invention relates to an additive which imparts detergent properties to mineral lubricating oils.

It is well known that the alkaline earth metal salts of alkylated phenol sulfides are effective as detergents and sludge dispersers for lubricating oils which are employed as crankcase lubricants for internal combustion engines. The preparation of calcium salts of this type and their use in lubricating oils are described in the Mikeska U. S. Patent 2,362,289. Similarly, barium salts are described in the Winning U. S. Patent 2,362,291, and the magnesium salts are described in the McNab U. S. Patent 2,362,292. Now we have discovered that mixed alkaline earth salts of alkylated phenol sulfides containing two alkaline earth metals are distinctly and surprisingly superior to the single salts in their detergent effects. For example, a mixed calcium and barium salt of tertiary octyl phenol sulfide in which the barium content is only about 15% of the total metal content on a molecular weight basis gives a much cleaner engine condition than a similar concentration of either the calcium salt or the barium salt.

In accordance with the present invention, mixed alkaline earth metal salts of alkylated phenol sulfides having at least one alkyl group of at least four carbon atoms attached to each benzene nucleus and containing two alkaline earth metals are employed as additives for mineral lubricating oils. For the purpose of this invention, the alkaline earth metal group includes calcium, barium, strontium, and magnesium. The presence of alkyl groups in the salts is necessary to impart sufficient oil solubility. The alkyl groups should contain at least four carbon atoms each and preferably contain from four to eight carbon atoms. The radicals may be straight chain or branched. The scope of the invention is not limited as to the number of sulfur atoms which interconnect the benzene nuclei, but compounds containing from one to four sulfur atoms in such linkage are preferred.

Methods of preparing alkylated phenol sulfides are well known and are described, for example, in the above-cited United States patents. The mixed metal salts of the present invention may be prepared by neutralizing a phenol sulfide with a mixture of basic compounds of the alkaline earth metals, e. g., the hydroxides; or they may be prepared by first partially neutralizing the phenol sulfide with one of the metals, and then completing the neutralization by treatment with a suitable basic compound of the other metal desired. Another method by which the mixed salts may be prepared consists in first preparing an alkali metal salt of the alkylated phenol sulfide and then reacting this salt with a mixture of alkaline earth metal salts, e. g., a mixture of the chlorides of the metals in question. For the best results, the proportion of metal compounds employed should be such that the final product contains at least 15% of each metal on a molecular basis, related to the total metal content of the salts.

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Methods of preparing various single metal and mixed metal salts of the alkaline earth metals and tests of the performance of lubricants containing such compounds are described in the following examples, which are intended to be illustrative only and not as limiting the scope of the invention in any way.

Example 1.—Calcium salt of tert.-octyl phenol sulfide

The following materials were blended together and added to a nickel reactor: 952 grams tert.-octyl phenol sulfide (prepared by alkylating phenol and diisobutylene and reacting the product with SCl_2), 152 grams stearyl alcohol, 1370 grams solvent extracted Mid-Continent paraffinic oil of 52 seconds viscosity Saybolt at 210° F. A slurry of 185 grams of commercial lime (CaO) and 500 grams of water were added to the product, and the whole mixture was heated with stirring at the reflux temperature for 24 hours. The reaction product was then removed, blown dry with nitrogen, and filtered through "Hi-flo" filter aid. Analysis showed the resulting concentrate to contain the following: Ash 8.09%, calcium 2.66%, sulfur 4.09%.

Example 2.—Strontium salt of tert.-octyl phenol sulfide

The following materials were blended together and added to a reaction flask: 468.5 grams tert.-octyl phenol sulfide (prepared as in Example 1), 81.4 grams stearyl alcohol, 732.0 grams of a solvent extracted Mid-Continent paraffinic oil of 52 seconds viscosity Saybolt at 210° F. 306 grams of strontium hydrate ($Sr(OH)_2.8H_2O$) was slowly added over a period of 2 hours to the mixture in the flask at 120° C. and then held at this temperature for an additional 4 hour period with rapid stirring. The contents of the flask was then dried by blowing with nitrogen at 150° C. and then filtered through "Hi-flo" filter aid. The product contained the following by analysis: Ash 14.11%, strontium 7.02%, sulfur 3.58%.

Example 3.—Barium salt of tert.-octyl phenol sulfide

The following materials were added to a reaction flask equipped with a water condenser and mechanical stirrer: 468.5 grams of tert.-octyl phenol sulfide (prepared as in Example 1), 39.2 grams stearyl alcohol, 802 grams solvent extracted Mid-Continent paraffinic oil of 52 seconds viscosity Saybolt at 210° F. The mixture was heated to 125° C. and 350 grams of barium hydrate, ($Ba(OH)_2.8H_2O$), added slowly over a period of 6 hours at 110–130° C. The product was dried by blowing with nitrogen for about one hour at 140° C., and filtered through "Hi-flo" filter aid. The product contained the following by analysis: Ash 15.27%, barium 9.31%, sulphur 3.27%.

Example 4.—Calcium-strontium salt of tert.-octyl phenol sulfide

1720 grams of the calcium salt concentrate prepared as described in Example 1, in which the calcium content was about 85% of the theoretical amount required to neutralize the alkyl phenol sulfide, was placed in a reaction flask and heated to 125° C. 84.5 grams of strontium hydrate ($Sr(OH)_2.8H_2O$), was added over a period of about 15 minutes and the mixture held at 125° C. with rapid stirring for 3¾ hours. The product was then blown with nitrogen gas for one hour, and then filtered through "Hi-flo" filter aid. Analysis showed it to contain the following: Ash 8.44%, calcium 2.63%, strontium 0.89%, sulfur 3.72%.

Example 5.—Calcium-barium salt of tert.-octyl phenol sulfide

1500 grams of the calcium salt concentrate prepared as in Example 1, containing about 85% of the theoretical amount of calcium required to neutralize the alkyl phenol sulfide, was placed in a reaction flask and heated to 125° C. 70 grams of barium hydrate ($Ba(OH)_2.8H_2O$) was added with rapid stirring over a period of 2½ hours. The mixture was then blown with nitrogen at 150° C. to dry the same and then filtered through "Hi-flo" filter aid. The product contained the following: Ash 10.17%, calcium 2.56%, barium 1.91%, sulfur 3.85%.

Example 6

In the following engine performance tests samples of an unblended base oil, consisting of a solvent extracted Mid-Continent paraffinic oil of SAE 30 viscosity grade, and of various blends consisting of this oil with the addition of 1% each of the various salts prepared as described in the preceding examples, were tested in a single cylinder Caterpillar engine, each run being made for 120 hours at 1000 R. P. M. with approximately 21 brake horse power output, an oil temperature of 145–150° F. and a jacket temperature of 175–180° F. At the end of each test the ring zone of the engine was inspected and given a demerit rating based on the condition observed. A demerit rating of zero represents a condition wherein there are no deposits, and a demerit rating of 10 represents the maximum deposit that can be formed in the test engine. Consequently, low demerit ratings indicate better engine conditions and hence a better performance of the oil in the engine. In preparing the blends for this test the concentrates described in the preceding examples were employed, each containing about 40% of the alkyl phenol sulfide salt. Amounts were

used to produce in each case a blend containing 1% of the salt. The results of these engine tests are shown in the following table:

Oil Blend	Ring Zone Demerit
Base Oil	1.91
Base Oil +1% calcium salt (product of Ex. 1)	1.47
Base Oil +1% strontium salt (product of Ex. 2)	0.92
Base Oil +1% barium salt (product of Ex. 3)	1.47
Base Oil +1% calcium-strontium salt (product of Ex. 4)	0.49
Base Oil +1% calcium-barium salt (product of Ex. 5)	0.83

The products of the present invention may be employed not only as the sole additives in hydrocarbon lubricating oils but also in conjunction with other detergent type additives such as metal sulfonates, metal soaps, metal phenates, metal alcoholates, metal phenol sulfonates, metal alkyl phenol sulfides, metal organo phosphates, thiophosphates, phosphites and thiophosphites, metal salicylates, metal xanthates and thioxanthates, metal thiocarbamates, amines and amine derivatives, reaction products of metal phenates or metal phenol sulfides with sulfur, reaction products of metal phenates or metal phenol sulfides with phosphorus sulfides, and the like. Thus, the new additives of this invention may be used in lubricating oils containing such addition agents as nickel oleate, barium octadecylate, calcium phenyl stearate, zinc diisopropyl salicylate, aluminum naphthenate, calcium cetyl phosphate, barium di-tert.-amyl phenol sulfide, calcium petroleum sulfonate, zinc methyl cyclohexyl thiophosphate, calcium dichlorostearate, etc.

The lubricating oil base stocks used in the compositions of this invention may be straight mineral lubricating oils, or distillates derived from paraffinic, naphthenic, asphaltic or mixed base crudes, or, if desired, various blended oils may be employed as well as residuals, particularly those from which asphaltic constituents have been carefully removed. The oils may be refined by conventional methods using acid, alkali and/or clay or other agents such as aluminum chloride, or they may be extracted oils produced, for example, by solvent extraction with solvents of the type of phenol, sulfur dioxide, furfural, dichlorodiethyl ether, nitrobenzene, crotonaldehyde, etc. Hydrogenated oils or white oils may be employed as well as synthetic oils prepared, for example, by the polymerization of olefins or by the reaction of oxides of carbon with hydrogen or by the hydrogenation of coal or its products. In certain instances cracking coil tar fractions and coal tar or shale oil distillates may also be used. Also, for special applications, animal, vegetable or fish oils or their hydrogenated or voltolized products may be employed, either alone or in admixture with mineral oils.

For the best results the base stock chosen should normally be that oil which without the new additives present gives the optimum performance in the service contemplated. However, since one advantage of the additives is that their use also makes feasible the employment of less satisfactory mineral oils or other oils, no strict rule can be laid down for the choice of the base stock. Certain essentials must of course be observed. The oil must possess the viscosity and volatility characteristics known to be required for the service contemplated. The oil must be a satisfactory solvent for the additive, although in some cases auxiliary solvent agents may be used. The lubricating oils, however they

may have been produced, may vary considerably in viscosity and other properties depending upon the particular use for which they are desired, but they usually range from about 40 to 150 seconds Saybolt viscosity at 210° F. For the lubrication of certain low and medium speed Diesel engines the general practice has often been to use a lubricating oil base stock prepared from naphthenic or aromatic crudes and having a Saybolt viscosity at 210° F. of 45 to 90 seconds and a viscosity index of 0 to 50. However, in certain types of Diesel service, particularly with high speed Diesel engines, and in gasoline engine service, oils of higher viscosity index are often required, for example up to 75 or 100, or even higher, viscosity index.

In addition to the materials to be added according to the present invention, other agents may also be used such as dyes, pour depressors, heat thickened fatty oils, sulfurized fatty oils, organo-metallic compounds, metallic or other soaps, sludge dispersers, antioxidants, thickeners, viscosity index improvers, oiliness agents, defoaming or antifoaming agents, resins, rubber, olefin polymers, voltolized fats, voltolized mineral oils, and/or voltolized waxes and colloidal solids such as graphite or zinc oxide, etc. Solvents and assisting agents, such as esters, ketones, alcohols, aldehydes, halogenated or nitrated compounds, and the like may also be employed.

Assisting agents which are particularly desirable as plasticizers and defoaming agents are the higher alcohols having eight or more carbon atoms and preferably 12 to 20 carbon atoms. The alcohols may be saturated straight or branched chain aliphatic alcohols such as octyl alcohol ($C_8H_{17}OH$), lauryl alcohol ($C_{12}H_{25}OH$), cetyl alcohol ($C_{16}H_{33}OH$), stearyl alcohol, sometimes referred to as octadecyl alcohol, ($C_{18}H_{37}OH$), and the like; the corresponding olefinic alcohols such as oleyl alcohol; cyclic alcohols, such as naphthenic alcohols; and aryl substituted alkyl alcohols, for instance, phenyl octyl alcohol, or octadecyl benzyl alcohol or mixtures of these various alcohols, which may be pure or substantially pure synthetic alcohols. One may also use mixed naturally occurring alcohols such as those found in wool fat (which is known to contain a substantial percentage of alcohols having about 16 to 18 carbon atoms) and in sperm oil (which contains a high percentage of cetyl alcohol); and although it is preferable to isolate the alcohols from those materials, for some purposes the wool fat, sperm oil or other natural products rich in alcohols may be used per se. Products prepared

synthetically by chemical processes may also be used, such as alcohols prepared by the oxidation of petroleum hydrocarbons, e. g., paraffin wax, petrolatum, etc.

The present invention is not to be considered as limited by any of the examples described herein, which are given by way of illustration only, but is to be limited solely by the terms of the appended claims.

We claim:

1. A mineral lubricating oil containing dissolved therein about 1% of a mixed alkaline earth metal salt of an alkylated phenol sulfide having an alkyl side chain of 4 to 8 carbon atoms attached to each benzene nucleus, the metal content of the salt consisting of 15% to 85% of calcium and 85% to 15% of a metal selected from the group consisting of barium and strontium, the percentages being molecular amounts, related to the total amount of metal required to neutralize the said alkylated phenol sulfide.

2. A composition according to claim 1 in which the alkyl side chains of the alkylated phenol sulfide are tertiary octyl groups.

3. A composition according to claim 2 in which the metal content of the salt consists of about 85% of calcium and about 15% of a metal selected from the group consisting of barium and strontium, on a molecular weight basis.

4. A composition according to claim 3 in which the salt contains about 85% of calcium and about 15% of barium on a molecular weight basis.

5. A composition according to claim 3 in which the salt contains about 85% of calcium and about 15% of strontium on a molecular weight basis.

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